

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improved Cementitious Compositions

We, SHAWINIGAN RESINS CORPORATION, a Corporation organised and existing under the laws of the Commonwealth of Massachusetts, United States of America, of Springfield, Commonwealth of Massachusetts, United States of America, (Assignee of VERA MYRA BIRTEN), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to cementitious compositions containing vinyl alcohol polymer resin binders. More particularly, this invention relates to compositions comprising a hydraulic cement, an inert particulate solid filler and an accelerator, the compositions being particularly suitable for structural application and coating compositions.

It has not heretofore been known to incorporate vinyl alcohol polymers in structural cementitious compositions comprising cement, an inert particulate solid filler and an accelerator. Although water soluble vinyl alcohol polymers would make useful air-entraining agents for such compositions because of an ability to foam extensively in aqueous solution, the general practice has been to refrain from the incorporation of these polymers in structural cementitious compositions. This exclusion has been the result of the tendency of vinyl alcohol polymers to prolong the setting time of the composition as well as reduce its hardness. To illustrate, polyvinyl alcohol has been suggested for addition to cement slurries used for "squeeze cementing" in oil well drilling operations, where the function of the polyvinyl alcohol is specifically to retard the setting time of the cement.

It has now been found that additions of vinyl alcohol polymers in controlled amounts to the present structural cementitious compositions do not deleteriously affect the setting time of the liquid dispersion or hardness of the cured product. Further, the curing characteristics of aqueous dispersions prepared from the present

cementitious compositions represent a major improvement, wherein the cast products obtained from such dispersions may be dry-cured, as distinct from the wet cure methods generally employed. Even further, the cured products have greatly improved tensile strength, flexural strength, and water tightness compared to products obtained from compositions not containing the vinyl alcohol polymer additive.

Accordingly, the present invention provides compositions containing 100 parts by weight of a hydraulic cement, 1—10 parts by weight of a water soluble vinyl alcohol polymer, 50—300 parts by weight of an inert particulate solid filler and 1—3 parts by weight of an accelerator. Various other agents may be incorporated in the described compositions in relatively minor amounts for the purpose of obtaining even further improvements.

The invention is further illustrated in the following examples. Where parts and percentages appear hereinafter in the specification they are parts and percentages by weight unless otherwise specified.

EXAMPLE 1

A powdered general purpose hydraulic cement mix was prepared having the following composition:

	Parts	75
Hi-early Portland cement	100	
Sand (crushed quartz, 85 mesh)	200	
Accelerator (calcium chloride)	2½	
Polyvinyl alcohol (low viscosity 87% to 89% hydrolyzed grade)	7	80

The dry ingredients in the above composition were mixed in a pebble mill at room temperature for approximately one half hour and yielded a free-flowing homogeneous powdered composition. When 75 parts of water were added to the powdered composition at room temperature and with agitation, the resulting liquid dispersion was a smooth uniform mechanically stable composition which could be easily hand-troweled.

EXAMPLES 2—14
To illustrate the advantages gained from the incorporation of certain other additives into the basic composition heretofore disclosed, 5 the following dry powdered admixtures were prepared according to the method of Example 1, having the proportion shown in Table 1 below. The cured products obtained from 10 aqueous dispersions of the compositions shown therein are particularly suitable for underlayments and masonry surface coatings.

TABLE 1

Examples

	2	3	4	5	6	7	8	9	10	11	12	13	14
Cement (Portland)	100	100	100	100	100	100	100	100	100	100	100	100	—
Cement (calcium-aluminate)	—	—	—	—	—	—	—	—	—	—	—	—	100
Sand (85 mesh, crushed quartz)	—	200	200	200	200	200	200	—	100	100	100	100	100
Marble dust (CaCO ₃)	200	—	—	—	—	—	—	200	—	—	—	—	—
Polyvinyl alcohol	—	—	7	7	7	7	7	7	2	2	2	2	7
Accelerator (alkali chloride)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.8	2.8	2.8	2.8	1
Borax	0.07	0.07	0.07	—	—	—	0.07	0.07	—	—	—	—	—
Boric Acid	—	—	—	0.09	—	—	—	—	—	—	—	—	—
Plasticizer (phosphoric acid ester)	1.2	1.2	—	1.2	—	1.2	1.2	1.2	—	—	—	—	1.2
Dispersing agent (sodium salt of polyvinyl alkyl, aryl sulfonic acid)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.6	0.6	0.6	0.6	0.8
Extender filler (talc)	5	5	5	5	5	5	5	5	5	5	5	5	—
Beryl stearate	—	—	—	—	—	—	—	—	—	2	—	—	—
Pozzolan (volcanic ash)	—	—	—	—	—	—	—	—	—	—	—	10	—
Alkali silicate (27½% Na ₂ O/55% SiO ₂)	—	—	—	—	—	—	—	—	1.4	—	—	—	—
Silicon (sodium methyl silicate)	—	—	—	—	—	—	—	—	—	—	0.7	—	—

Although the method of mixing dry ingredients comprising the basic composition of the present invention is not critical, the method of incorporating certain of the additives shown above must be controlled in order to yield compositions having the improved properties stated. For example, in the above compositions containing borax, because of the relatively minor amounts used compared to the other dry ingredients it is necessary to first dissolve the borax in an inert solvent which will not react with the cement constituent and then disperse uniformly the solution in the other dry ingredients of the admixture. The solvent used for the solution of the borax may conveniently be the liquid plasticizer for the vinyl alcohol polymer, in those instances where a plasticizer is used. The borax should not be contacted directly with the vinyl alcohol polymer during the preparation of the dry admixture since contact will promote the premature gelation of the polymer when water is added to make up the aqueous dispersion. Also, when liquid plasticizers are incorporated into the dry admixture, as shown in the above examples, the plasticizer should first be dispersed in an inert solid carrier, preferably the filler, to minimize agglomeration and attendant inhomogeneity.

Aqueous dispersions were prepared from the compositions of Examples 2—9 merely by mixing the dry admixture with from one quarter to one third of the weight of the admixture of water. The liquid dispersions were cast into test bars and air-cured for the purpose of determining the improved physical properties of the present compositions. The

test bars were prepared corresponding to the appropriate ASTM specifications.

Dumbell specimens measuring 3" overall length, 1 $\frac{1}{8}$ " overall width and 1" thickness were tested for tensile strength according to ASTM C190—49. Bar specimens of 2" x 2" x 12" dimensions were measured for flexural strength and deflection according to ASTM C348—54T. All samples containing the vinyl alcohol polymer were dry cured, that is to say, after casting the sample was permitted to air dry under usual ambient indoor conditions. The test bars prepared from the compositions not containing the vinyl alcohol polymer were wet cured, a procedure which requires that the surface of the specimen after casting be continually kept moist with water during the entire setting period. The tensile strength, flexural strength and flexibility measurements were made on a standard Instron Tester (Instron is a Registered Trade Mark).

The amount of water absorbed by the test specimen after cure was measured to determine the water tightness of a particular cured composition. The test was conducted by first immersing the test specimen totally in water for a period of 24 hours, thereafter removing the specimen and wiping all surface water droplets therefrom by means of a towel and immediately weighing the specimen. The difference in weight between the immersed specimen and the dry specimen was calculated as percent moisture absorbed on a weight basis.

All tests were made after a cure period of 28 days, and the results are in Table 2 below.

TABLE 2

Example	Type Type Cure	Tensile Strength (psi)	Flexural Strength (psi)	Deflection (inches/ 6 inch)	Water Absorption (%)
2	Wet	361	455	0.023	19.0
3	Wet	558	1083	0.030	6.5
4	Dry	845	1350	0.051	4.9
5	Dry	468	1500	0.037	10.0
6	Dry	950	1363	0.047	4.8
7	Dry	978	1440	0.114	4.0
8	Dry	880	1463	0.041	6.5
9	Dry	400	608	0.036	17.0

It will be noted from the above results that the compositions containing the vinyl alcohol polymer had greatly improved strength, flexibility and water tightness when compared to

like compositions not containing the vinyl alcohol polymer. The improved results were obtained for the present compositions containing polyvinyl alcohol even though the con-

trol samples were given a wet cure, which latter treatment promotes greater strength and water tightness for a given composition. It should also be noted that the compositions containing borax and/or plasticizer in addition to the vinyl alcohol polymer gave improved flexural strength compared to the composition containing the vinyl alcohol polymer without other additives.

10 The composition containing alkali silicate shown in Example 10, when tested for water tightness according to the method previously described, absorbed 8% water after a 7 day cure compared to 10% absorption for the composition containing polyvinyl alcohol alone.

15 The composition containing alkali silicate shown in Example 11 above absorbed 4.7% moisture for the same test. The silicon containing composition shown in Example 12 absorbed 8% moisture. The pozzolan containing composition of Example 13, also absorbed 8% moisture.

20 The calcium-aluminate cement composition of Example 14 is particularly suitable for application where it is desired to adhere the cured cement product to a metal substrate. It has not heretofore been possible to adhere a cementitious composition containing this type hydraulic cement to a metal substrate satisfactorily. It has now been found that calcium-aluminate cement compositions may be adhered to most common metal substrates merely by the incorporation of a vinyl alcohol polymer according to the present invention.

35 Suitable vinyl alcohol polymers for use in the present compositions may be substantially water soluble copolymers of vinyl alcohols with other monomers of the type that are copolymerizable with vinyl esters, the vinyl alcohol polymer being further characterized by an ability to undergo gel formation in an aqueous cementitious dispersion. Useful polymers may be a copolymer formed by the hydrolysis of a vinyl ester homopolymer as well as terpolymers formed by the copolymerization of a vinyl ester with another copolymerizable monomer and the further hydrolysis product thereof. For example, the useful vinyl ester homopolymers which may be directly hydrolyzed to yield a substantially water soluble copolymer capable of gel formation in an aqueous cementitious dispersion include vinyl acetate, vinyl propionate, vinyl butyrate, vinyl hexoate and vinyl benzoate. As typical of the terpolymer type of vinyl alcohol polymer, wherein a copolymer of a vinyl ester is further hydrolyzed to yield a substantially water soluble polymer capable of gel formation in an aqueous cementitious dispersion there is included copolymers of a vinyl ester with esters of copolymerizable monoethylenically unsaturated dicarboxylic acids, such as dibutyl maleate, diethyl fumarate, and dioctyl maleate; copolymers of a vinyl ester with other vinyl esters such as the vinyl propionate, vinyl butyrate,

vinyl hexoate and vinyl benzoate copolymers of vinyl esters with vinyl halides, such as vinyl chloride and vinyl bromide; copolymers of a vinyl ester with lower alkyl esters of acrylic acid such as methyl acrylate, propyl acrylate, butyl acrylate, hexyl acrylate and octyl acrylate; copolymers of vinyl acetate with lower alkyl esters of methacrylic acid such as methyl methacrylate, propyl methacrylate, butyl methacrylate, hexyl methacrylate and octyl methacrylate; copolymers of a vinyl ester with monoethylenically unsaturated carboxylic acids, such as acrylic acid, methacrylic acid and crotonic acid; copolymers of vinyl esters with other ethylenic monomers such as ethylene and propylene.

The preferred type of vinyl alcohol polymer is the copolymer of vinyl acetate with vinyl alcohol formed by the direct hydrolysis of polyvinyl acetate, which copolymer contains from 72% up to 100% hydrolyzed groups. The preferred copolymer is available commercially as polyvinyl alcohol and may be further characterized as having from 0 to 42% residual polyvinyl acetate groups and a viscosity of 1-65 centipoises for a 4% aqueous solution at 20°C. Especially preferred is polyvinyl alcohol having a viscosity of from 25 to 65 centipoises for a 4% aqueous solution at 20°C. for the reason that the cured cementitious composition containing these grades is more water resistant in the dry state and possesses greater strength and flexibility.

The useful inert particulate solid fillers for the present compositions are inorganic compounds that are relatively inert in aqueous cementitious dispersions and which may best be characterized by a particle size not exceeding that which will pass through a sieve with one quarter inch opening. 100 to 200 parts of such materials per 100 parts of cement are preferred. Many of the suitable inorganic compounds are mineral in nature and may be aggregate material used in concrete. The useful inert particulate solid fillers include such known inorganic compounds as crushed stone, paint pigments, pigment extenders, gravel, clays, texturing agents, sands, shales and slates. Mixtures of the inert particulate solid fillers are useful as demonstrated in the above examples where talc, a well known extender type material, was employed together with sand and marble dust. The extender type materials perform the additional function of workability agents to promote the ease of hand-trowelling the aqueous dispersion and include titanium dioxide, calcium silicates, micas, silica, calcium carbonate, aluminium silicate, and magnesium silicate which extenders may be characterized by a particle size not exceeding 20 microns average diameter. The useful range for the extender type inert particulate solid filler is 1 to 20 preferably 5-20 parts by weight per 100 parts by weight cement: A range of 1 to 20 parts by weight per 100

parts of cement is particularly preferred when alkali metal silicates are employed.

The useful accelerators are well known and may be substantially water soluble alkali and alkaline earth metal halides including calcium chloride, sodium chloride and lithium chloride. It is the practice in the art to employ calcium chloride for Portland type hydraulic cements, but to employ lithium chloride in the preparation of calcium alumina type hydraulic cement compositions.

The selection of a dispersing agent for the present compositions is not critical and suitable dispersing agents may be anionic, cationic and non-ionic surface active agents. Preferred dispersing agents of the cationic type are tertiary amines; of the anionic, the following are preferred: sulposuccinates, and alkyl aryl sulphonates; preferred non-ionic dispersing agents are the ethylene oxide-fatty acid condensates, the alkyl aryl alcohols, polyoxyalkylene compounds such as polypropylene oxide-polyethylene oxide block copolymer. The permissible range for the dispersing agent where one is employed is 0.5—5 parts by weight per 100 parts by weight of cement.

The useful pozzolan materials which may be employed in the present compositions are defined in the United States Department of the Interior Publication "Concrete Manual", page 47, 6th edition, 1956, as follows: "pozzolans are siliceous or siliceous and aluminous materials, which in themselves possess little or no cementitious value, but will in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties". Suitable pozzolan materials include those of a volcanic origin such as volcanic ash and piccolo as well as those of an industrial origin such as slags, fly ash and the silico-fluoride types. The permissible range for the pozzolanic materials is 1—30 parts by weight per 100 parts by weight cement in the composition.

The stearates which may be employed in the present compositions for the improvement of water tightness of the cured product can be used in proportions of 1—8 parts by weight per 100 parts by weight of cement. The butyl stearate employed in the preceding example is especially preferred for the additional reason that the presence of this material in the aqueous dispersion containing a vinyl alcohol polymer minimizes any undesirable foaming tendencies of the dispersion.

Effective plasticizers which may be employed for the vinyl alcohol polymers used in the present compositions are well known and may be water soluble organic compounds which are compatible with the vinyl alcohol polymer. Especially preferred plasticizers include the phosphoric acid esters used in the preceding examples, glycerin-formamide, glycerin, the

lower glycols generally, and hydroxylated amides. The useful range for the plasticizer is up to 60 parts preferably 5 to 30 parts by weight plasticizer per 100 parts by weight of the vinyl alcohol polymer.

The amount of borax which may be employed in the present compositions containing the vinyl alcohol polymer is critical to avoid the premature gelation of the vinyl alcohol polymer in the aqueous cementitious dispersion. The critical range is 0.2—3.0 parts by weight of borax per 100 parts by weight of the vinyl alcohol polymer. Although it is believed by the applicants that boron salts other than borax can be used in substitution for the borax, it has been learned that the substitution of boric acid for borax produces undesirable results, namely, the lowering of tensile strength and increase in water absorption of the cured product.

The useful amount of silicon in the present compositions for the purpose of improving the water impermeability of the cured product is from 0.7—3.0 parts by weight silicon per 100 parts by weight of cement.

It is not intended to limit the present compositions for use in structural applications, such as the general cement mix and underlayment compound appearing in the foregoing examples. It is obvious that such compositions may be modified merely by the incorporation of a pigment and thereby obtain an improved cement paint. Also, other known additives for cementitious compositions generally may be incorporated in the present compositions, such as the alkali silicates and silicones used in the preceding examples and such others as for example, air-entraining agents, retarders and solvents. It is further not intended to limit the aqueous dispersions of the present invention to the amount of water added in the preceding examples, since, for coating composition applications the water content may be varied over a wide range without detrimental influence on the final properties of the cured product.

A typical composition within the scope of the present invention comprises 100 parts of a Portland cement, 100—200 parts sand, 1—3 parts of an accelerator, 1—10 parts polyvinyl alcohol, 5—20 parts of an inert inorganic extender having an average particle diameter not exceeding 20 microns, 2—20 parts of a dispersing agent, 5—30 parts of a plasticizer per 100 parts polyvinyl alcohol, and 0.2—3.0 parts borax per 100 parts polyvinyl alcohol.

Another typical composition within the scope of the present invention comprises 100 parts of a Portland cement, 100—200 parts marble dust, 1—3 parts of an accelerator, 1—10 parts polyvinyl alcohol, 5—20 parts of an inert inorganic extender having an average particle diameter not exceeding 20 microns, 2—20 parts of a dispersing agent, 5—30 parts of a

plasticizer per 100 parts polyvinyl alcohol and 0.2—3.0 parts borax per 100 parts polyvinyl alcohol.

WHAT WE CLAIM IS:—

1. A dry powdered admixture comprising 100 parts by weight of a hydraulic cement 50 to 300 parts by weight of an inert particulate solid filler, 1 to 3 parts by weight of an accelerator and 1 to 10 parts by weight of a water soluble vinyl alcohol polymer.

2. An admixture as claimed in Claim 1 in which the hydraulic cement is Portland cement.

3. An admixture as claimed in Claim 1 or 2 in which the water soluble vinyl alcohol polymer is polyvinyl alcohol.

4. An admixture as claimed in any of Claims 1 to 3 in which the water soluble vinyl alcohol polymer is a co-polymer of vinyl-acetate with vinyl alcohol formed by hydrolysing polyvinyl acetate which copolymer contains 72% to 100% hydrolysed groups.

5. An admixture as claimed in any of Claims 1 to 3 in which the water soluble vinyl alcohol polymer is a polyvinyl alcohol having 0 to 42% residual polyvinyl acetate groups and a viscosity of 1 to 65 centipoises for a 4% aqueous solution at 20°C.

6. An admixture as claimed in Claim 5 in which the polyvinyl alcohol has a viscosity of 25 to 65 centipoises for a 4% aqueous solution at 20°C.

7. An admixture as claimed in any of preceding claims in which the accelerator is a water soluble alkali metal or alkaline earth metal halide.

8. An admixture as claimed in any of the preceding claims in which the inert particulate solid filler has a particle size such that it will pass through a sieve with $\frac{1}{4}$ inch size openings.

9. An admixture as claimed in any of the preceding claims in which sufficient of the filler is replaced by an extender so that 5—20 parts by weight of said extender are present for each 100 parts of cement.

10. An admixture as claimed in Claim 9 in which the average particle diameter of the extender does not exceed 20 microns.

11. An admixture as claimed in Claims 9 or 10 in which the extender is talc.

12. An admixture as claimed in any of the preceding claims which contains 1 to 30 parts by weight of pozzolans per 100 parts by weight of the cement.

13. An admixture as claimed in Claim 12 in which the pozzolan is volcanic ash, piccolo, slags, flyash or of the silicofluoride type.

14. An admixture as claimed in any of the preceding claims which contains 1 to 8 parts by weight of a stearate per 100 parts by weight of the cement.

15. An admixture as claimed in Claim 14 in which the stearate is butyl stearate.

16. An admixture as claimed in any of the preceding claims in which a dispersing agent

is present in an amount 0.5 to 5 parts by weight per 100 parts by weight of cement.

17. An admixture as claimed in Claim 16 in which the dispersing agent is a tertiary amine, a sulphosuccinate, an alkyl aryl sulphonate, an ethylene oxide-fatty acid condensate or aryl alkyl alcohol or a polyoxy-alkylene compound.

18. An admixture as claimed in any of the preceding claims in which there is present a plasticizer for the vinyl alcohol polymer in an amount of up to 60 parts by weight per 100 parts by weight of vinyl alcohol polymer.

19. An admixture as claimed in Claim 18 in which the plasticizer is a phosphoric acid ester, glycerin-formamide, or lower glycol or a hydroxylated amide.

20. An admixture as claimed in any of the preceding claims in which there is present 0.2 to 3.0 parts by weight of borax per 100 parts by weight of vinyl alcohol polymer.

21. An admixture as claimed in any of the preceding claims in which there is present 0.7 to 3.0 parts by weight of a silicon per 100 parts by weight of cement.

22. An admixture as claimed in any of the preceding claims in which there is present 1 to 20 parts by weight of an alkali metal silicate per 100 parts by weight of cement.

23. A dry powdered admixture comprising 100 parts of a Portland cement, 100—200 parts sand, 1—3 parts of an accelerator, 1—10 parts polyvinyl alcohol, 5—20 parts of an inert inorganic extender having an average particle diameter not exceeding 20 microns, 2—20 parts of a dispersing agent, 5—30 parts of a plasticizer per 100 parts polyvinyl alcohol, and 0.2—3.0 parts borax per 100 parts polyvinyl alcohol.

24. A dry powdered admixture comprising 100 parts of a Portland cement, 100—200 parts marble dust, 1—3 parts of an accelerator, 1—10 parts polyvinyl alcohol, 5—20 parts of an inert inorganic extender having an average particle diameter not exceeding 20 microns, 2—20 parts of a dispersing agent, 5—30 parts of a plasticizer per 100 parts polyvinyl alcohol and 0.2—3.0 parts borax per 100 parts polyvinyl alcohol.

25. An admixture as claimed in Claim 1 substantially as hereinbefore described.

26. An aqueous dispersion of the admixture as claimed in any of the preceding claims.

27. An air-cured product of the aqueous dispersion as claimed in Claim 26.

28. The process of preparing a dry powdered admixture as claimed in any of Claims 1 to 25 capable of forming a solid air-cured product having improved strength and flexibility from an aqueous dispersion thereof, which comprises dry blending 100 parts of a hydraulic cement, 50—300 parts of an inert particulate solid filler, 1—3 parts of an accelerator and 1—10 parts of a water soluble vinyl alcohol polymer.

29. The process of preparing an aqueous cement dispersion as claimed in Claim 26 which can be air-cured to form a solid product having improved strength and flexibility 5 which comprises mixing with the normal amount of water, a dry powdered admixture comprising 100 parts of hydraulic cement, 50—300 parts of an inert particulate solid filler, 1—3 parts of an accelerator and 1—10 parts of a water soluble vinyl alcohol polymer. 10
30. The process for preparing a dry powdered admixture as claimed in Claim 1 or an aqueous dispersion thereof as claimed in Claim 26 substantially as hereinbefore de- 15 scribed.

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